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$ZnO–SnO_2$ transparent conductive films deposited by opposed target sputtering system of ZnO and SnO_2 targets

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Abstract

Thin $ZnO–SnO_2$ films were deposited on glass substrates by opposed planar magnetron sputtering, in which ZnO and SnO_2:Sb (Sb_2O_5 3 wt% doped) targets face each other. Glass substrate temperatures (T_s) were held at 150°C and 250°C. As an experimental parameter, current ratio δ, ZnO target current divided by the sum of ZnO and SnO_2 target currents, was used. Compositions of as-deposited film were changed with the current ratio δ. Amorphous transparent films appeared over the range of $0.47 \leqslant \delta \leqslant 0.80$ ($Zn/(Zn+Sn) = 0.28–0.76$) at $T_s = 150°C$, over the range of $0.33 \leqslant \delta \leqslant 0.73$ ($Zn/(Zn+Sn) = 0.32–0.66$) at $T_s = 250°C$. Crystalline $ZnSnO_3$ and crystalline Zn_2SnO_4 was not obtained in any of the as-deposited films, even at $\delta = 0.62$ ($Zn/(Zn+Sn) = 1/2$) or $\delta = 0.73$ ($Zn/(Zn+Sn) = 2/3$). Amorphous films exist as form of $(ZnSnO_3)_{1-x}(SnO_2)_x$ over the range of $0.50 \leqslant \delta \leqslant 0.62$ ($0 \leqslant x \leqslant 0.5$) and $(ZnSnO_3)_{1-y}(ZnO)_y$ over the range of $0.62 \leqslant \delta \leqslant 0.73$ ($0 \leqslant y \leqslant 0.5$). The minimum resistivity of the deposited amorphous films was $3.6 \times 10^{-2}\,\Omega$cm at $\delta = 0.50$ ($Zn/(Zn+Sn) = 0.33$), $T_s = 250°C$.

Keywords: Transparent conductive film; ZnO; SnO_2; Sputtering; Amorphous; $ZnSnO_3$; Zn_2SnO_4

1. Introduction

Transparent Conductive oxide (TCO) films are necessary in applications such as transparent electrodes for solar cells, flat panel displays and window coatings [1,2]. At present, indium tin oxide (ITO) is mainly used in TCO materials, because of the low resistivity and low optical absorptance in the visible spectrum. Previously, $ZnO–In_2O_3$ thin films have been deposited by simultaneous DC sputtering at $T_s = 150°C$ [3–6]. Amorphous phase films exhibit a minimum resistivity of $2.3 \times 10^{-4}\,\Omega$cm and have potential applications in TCO films. To explore other compound films, experiments were conducted with In_2O_3 replaced by SnO_2. In the $ZnO–SnO_2$ system, two compounds have been reported in TCO films, the ilumenite $ZnSnO_3$ and the spinel Zn_2SnO_4 [2,7,8]. In this study, films of all compositional ratios of $Zn/(Sn+Zn)$ were deposited. Film structures were first examined by XRD, in particular the presence

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of amorphous phase in the ZnO–SnO_2 system. Electrical and optical properties were examined next. The effects of annealing the amorphous films on structural property were also investigated in Ar gas.

2. Experimental

An Opposed target sputtering system was used to deposit ZnO–SnO_2 films. Fig. 1 shows a schematic diagram of the system. A ZnO target and an SnO_2:Sb target doped with 3 wt% Sb_2O_5 face each other by a distance of 10 cm. These targets were held on target holders, which contain permanent ferrite magnet arrays to produce strongly unbalanced planar magnetron sputtering. Sputtering was performed at 0.133 Pa (1 mTorr) in pure Ar for 2 h. Corning 7059 glass substrate temperatures (T_s) were held at 150°C and 250°C. Discharge currents for ZnO and SnO_2:Sb are denoted as I_{Zn} and I_{Sn}, respectively. The current ratio $\delta = I_{Zn}/(I_{Sn} + I_{Zn})$ was varied as a parameter of deposition. For $0 \leqslant \delta \leqslant 0.5$, I_{Sn} was fixed at 80 mA and I_{Zn} was varied from 0 to 80 mA, whereas at $0.5 \leqslant \delta \leqslant 1$, I_{Zn} was fixed at 80 mA and I_{Sn} was varied from 80 mA to 0.

Compositional ratios Zn/(Zn + Sn) of the deposited films were estimated by X-ray fluorescence measurements. Compositional ratio increased with increasing δ but was slightly smaller than the value of δ. Values of Zn/(Zn + Sn) = 1/2 and 2/3 corresponded to $\delta = 0.62$ and 0.73, respectively.

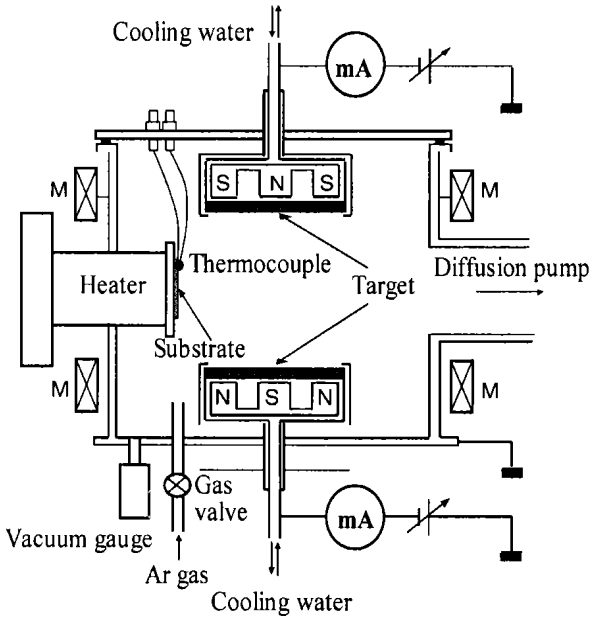

Fig. 1. Schematic drawing of the DC-magnetron sputtering system.

3. Results and discussion

Fig. 2 shows compositional ratios of Zn/(Zn + Sn) as a function of δ for films deposited at 250°C. The deposition of ZnO was less than that of SnO_2. Values of δ corresponding to the composition of ilumenite-like $ZnSnO_3$ and spinel-like Zn_2SnO_4 were 0.62 and 0.73, respectively.

X-ray diffraction patterns for films deposited at $T_s = 250$°C are shown in Fig. 3 as a function of δ. Diffraction patterns for $0 \leqslant \delta \leqslant 0.47$ indicate that the films consist mainly of rutile SnO_2 phase by comparison with JCPDS cards. At $0.38 \leqslant \delta \leqslant 0.47$ the signals are weaker and broader. This indicates that amorphous phase of some kind is included in rutile SnO_2 as ZnO content increases. Diffraction patterns for $0.50 \leqslant \delta \leqslant 0.73$ exhibit no definite peaks, indicating that the films are amorphous in structure. Neither $ZnSnO_3$ nor Zn_2SnO_4 crystalline phase was observed at $\delta = 0.62$ and 0.72, where

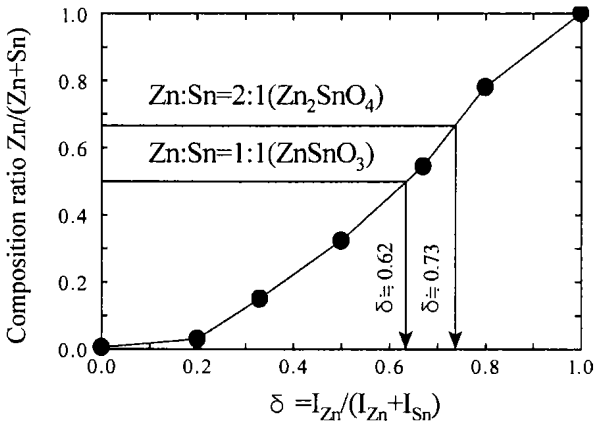

Fig. 2. The composition ratio for ZnO–SnO_2 films deposited at $T_s = 250$°C as a function of δ.

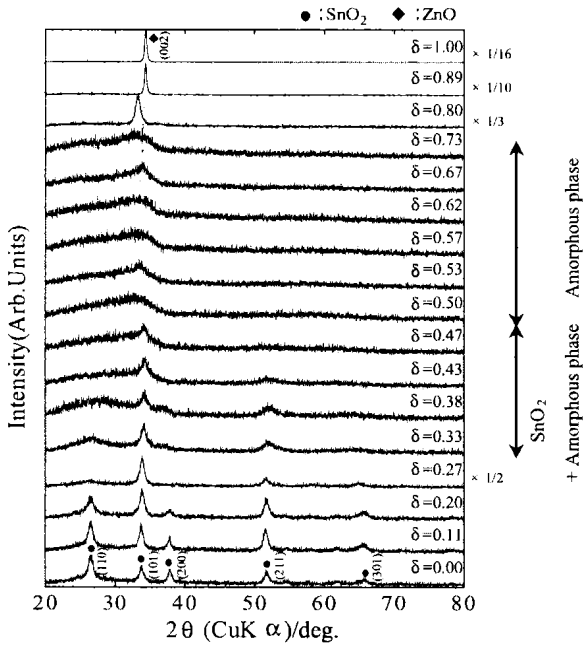

Fig. 3. X-ray diffraction patterns for films deposited at $T_s = 250°C$ as a function of δ. Magnification of diffraction intensity for $\delta = 0.27$, 0.80, 0.89 and 1.00 is shown at the right margin of the figure.

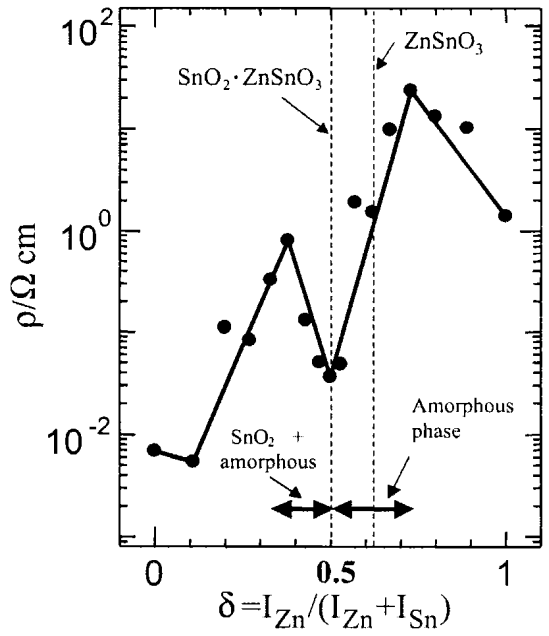

Fig. 4. Resistivities of the films deposited at $T_s = 250°C$ as a function of δ.

the appearance of stoichiometric films was expected. At $\delta = 0.80$, a strong peak appeared nearly $2\theta \approx 33°$. This peak could not be identified from the JCPDS cards of ZnO and SnO_2, although identification is not definite at the present stage. XRD pattern for films of $0.83 \leqslant \delta \leqslant 1.00$ indicate wurtzite ZnO. XRD patterns of films deposited at $T_s = 150°C$ are almost the same as those deposited at $T_s = 250°C$. An amorphous phase appeared in the range of $0.47 \leqslant \delta \leqslant 0.80$ at 150°C.

Fig. 4 shows the resistivities of the films deposited at $T_s = 250°C$ as a function δ. The minimum resistivity was $5.4 \times 10^{-3}\Omega$cm at $\delta = 0.11$. This film was thought to be rutile SnO_2 doped with ZnO. Further ZnO doping of SnO_2 led to a rapid increase in film resistivity. As amorphous phase becomes mixed with rutile SnO_2 at $0.38 \leqslant \delta \leqslant 0.50$ film resistivity decreases with increasing Zn content. At $\delta = 0.50$ where the diffraction peaks corresponding to SnO_2 disappeared completely, film resistivity reached a minimum of $3.6 \times 10^{-2}\Omega$cm. The trend in resistivity at $0.38 \leqslant \delta \leqslant 0.50$ would be a consequence of changing the ratio of the rutile SnO_2 phase with high resistivity to the amorphous phase seen at $\delta = 0.50$. Resistivity then increased again with increasing Zn content up to $\delta = 0.73$ where the composition ratio Zn/(Zn + Sn) corresponds to the spinel Zn_2SnO_4.

The presence of a minimum resistivity as composition changed has also been reported by Minami et al. [7], where $ZnSnO_3$ was formed at the minimum resistivity. In our films, the composition of the film at $\delta = 0.50$ having the minimum resistivity deviated from that of $ZnSnO_3$. The composition ratio of Zn/(Zn + Sn) is nearly equal to 1/3. This corresponds to $ZnSn_2O_5$. The film with a composition ratio corresponding to $ZnSnO_3$ was deposited at $\delta = 0.62$, much higher than minimum resistivity. Therefore, amorphous $ZnSnO_3$ and SnO_2 can be presumed to be mixed. Amorphous films exist in the forms of $(ZnSnO_3)_{1-x}(SnO_2)_x$ over the range of $0.50 \leqslant \delta \leqslant 0.62$ $(0 \leqslant x \leqslant 0.5)$ and in the form of $(ZnSnO_3)_{1-y}(ZnO)_y$ over the range of $0.62 \leqslant \delta \leqslant 0.73$ $(0 \leqslant y \leqslant 0.5)$. Amorphous SnO_2 or ZnO were

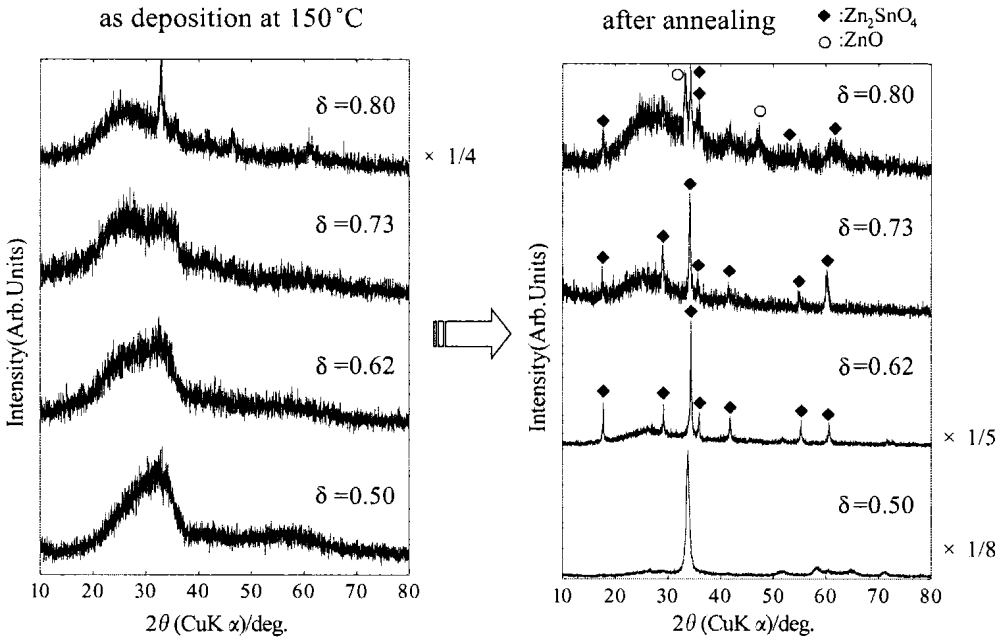

Fig. 5. X-ray diffraction patterns as -deposited and after annealing of amorphous phase films at $T_s = 150°C$ for 1 h in Ar gas at 650°C. Magnification of diffraction intensity is shown at the right margin of each figure.

highly dispersed throughout the amorphous $ZnSnO_3$.

For films containing amorphous phase, at $0.50 \leqslant \delta \leqslant 0.73$, the carrier concentration of this system is thought to be generated from oxygen vacancies in the zinc–stannate lattice, as suggested by Minami et al. [7] Their data shows that more oxygen vacancies in amorphous $ZnSnO_3$ are generated by excess Sn. In our data in Fig. 4, excess SnO_2 in $ZnSnO_3$ is thus expected to attract more oxygen in the $ZnSnO_3$. It is also found that excess ZnO in $ZnSnO_3$ attracts less oxygen in the $ZnSnO_3$ from the data in Fig. 4. These will be ascribed to the affinity of excess SnO_2 or ZnO to oxygen in $ZnSnO_3$. The same trends in resistivity could be observed for the films deposited at $T_s = 150°C$.

Fig. 5 shows X-ray diffraction patterns after annealing of amorphous phase films deposited at $T_s = 150°C$ in Ar gas at 650°C Peaks corresponding to Zn_2SnO_4 appeared in the films of $0.62 \leqslant \delta \leqslant 0.80$. This seems to be due to decomposition of $ZnSnO_3$ into Zn_2SnO_4 and SnO_2 during annealing [9]. This confirms the presence of $ZnSnO_3$ in the amorphous-phase film. Though resistivity of film deposited at $\delta = 0.50$ decreased slightly, amorphous films deposited at larger δ values in Fig. 5 showed increasing resistivity after annealing.

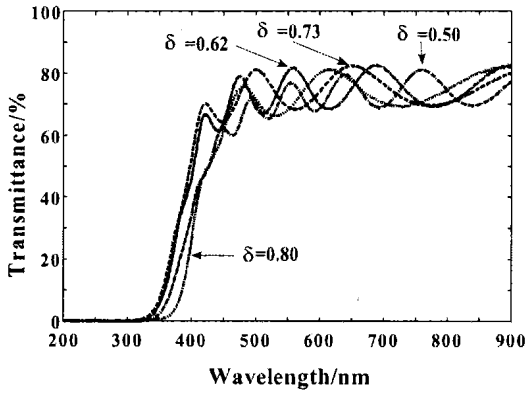

Fig. 6. Optical transmission spectra for films deposited at $T_s = 250°C$ as a function of δ.

Optical transmission spectra of films deposited at $T_s = 250°C$ in the amorphous region are shown in Fig. 6 as a function of δ. Optical transparencies of the amorphous films were 70–90% in the visible region, higher than those for $T_s = 150°C$ films. Estimate of the optical bandgap energies of the films from these optical transmission spectra ranged from 3.3 to 3.6 eV. The amorphous $ZnSnO_3$ at $\delta = 0.63$ and Zn_2SnO_4 at $\delta = 0.72$ gave the largest value of 3.6 eV. Optical bandgap energy of the amorphous film at minimum resistivity was 3.47 eV. Further addition of SnO_2 to $ZnSnO_3$ increased the band tailing.

4. Conclusion

Amorphous Phase in the ZnO–SnO_2 system were observed in films deposited by simultaneous sputtering at $T_s = 150°C$ and 250°C Amorphous transparent films appeared for $Zn/(Zn+Sn) = 0.28$–0.76 at $T_s = 150°C$, in $Zn/(Zn+Sn) = 0.32$–0.66 at $T_s = 250°C$. The presence of both amorphous SnO_2 and $ZnSnO_3$ could have an important role in the reduction of resistivity. The presence of both amorphous ZnO and $ZnSnO_3$ induced an increase in resistivity. These amorphous films exhibited minimum resistivity at $Zn/(Zn+Sn) = 0.33$ ($\delta = 0.50$), $T_s = 250°C$ which indicates that the film is composed of a mixture of amorphous $ZnSnO_3$ and SnO_2.

Acknowledgements

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